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Remarkable Effects of Aluminum Cocatalyst and Comonomer in Ethylene Copolymerizations Catalyzed by (Arylimido)(aryloxo)vanadium Complexes: Efficient Synthesis of High Molecular Weight Ethylene/Norbornene Copolymer

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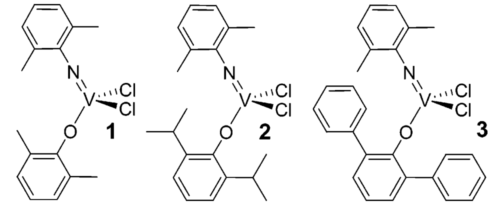
ABSTRACT: Copolymerizations of ethylene with norbornene (NBE), cyclopentene (CPE) and 1-hexene by (arylimido)(aryloxo)vanadium(V) complexes of the type VCl$_2$(N-2,6-Me$_2$C$_6$H$_3$)(OAr) [Ar = 2,6-Me$_2$C$_6$H$_3$ (**1**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**), 2,6-Ph$_2$C$_6$H$_3$ (**3**)] with cocatalyst [methylaluminoxane (MAO) or Et$_2$AlCl] catalyst systems have been explored. These complexes exhibited remarkable catalytic activities for ethylene polymerization in the presence of Et$_2$AlCl cocatalyst; in particular, the resultant polyethylene prepared by **1** possessed narrow molecular weight distributions and the M_n value increased linearly upon increasing the polymer yields (TON values). Notable effects of Al cocatalyst have been observed in the copolymerization of ethylene with NBE: the catalytic activities, the NBE incorporation, dominant chain transfer reactions, and the M_n values for resultant copolymers were highly dependent upon the Al cocatalyst employed (MAO or Et$_2$AlCl). The **1**−Et$_2$AlCl catalyst system exhibited remarkable catalytic activities, affording ultrahigh molecular weight poly(ethylene-*co*-NBE)s with narrow molecular weight distributions ($M_n = 2.12-2.70 \times 10^6$, $M_w/M_n = 1.29-1.53$), and the M_n values were independent upon the NBE contents but were dependent upon the Al/V molar ratios. In contrast, **1**−MAO catalyst exhibited better NBE incorporation than the **1**−Et$_2$AlCl catalyst, and the M_n value was independent of the Al/V molar ratio but was dependent upon the NBE contents. Modification of the aryloxide ligand affected the catalytic activity, but it did not strongly affect the NBE incorporation, the M_n values, and microstructure in the resultant copolymers. However, **1** exhibited a negligible amount of CPE incorporation in the ethylene/CPE copolymerization and also exhibited inefficient 1-hexene incorporation in the ethylene/1-hexene copolymerization. Since the resultant polymer obtained by the attempted copolymerization of ethylene with styrene was polyethylene, the effect of comonomer toward both the catalytic activity and the comonomer incorporation has been demonstrated.

Introduction

Topics concerning precise synthesis of polyolefins by new generation of transition metal catalysis attract considerable attention,[1] because the evolution of new polyolefins that have never been prepared by ordinary catalysis is thus highly anticipated. Since the classical Ziegler type vanadium catalyst systems displayed unique characteristics[2−5] such as (a) synthesis of a high molecular weight polymer with narrow polydispersity,[3] (b) synthesis of an ethylene/α-olefin copolymer with high α-olefin content,[3a,4] (c) living polymerization[5] affording propylene−methyl methacrylate diblock copolymers,[5b] and (d) others,[6] therefore, the process of the design and synthesis of new vanadium complex catalysts directed toward controlled olefin polymerization has been one of the most attractive goals.

Chart 1



We reported recently that (arylimido)(aryloxo)vanadium(V) complexes of the type VCl$_2$(N-2,6-Me$_2$C$_6$H$_3$)(OAr) [Ar = 2,6-Me$_2$C$_6$H$_3$ (**1**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**), 2,6-Ph$_2$C$_6$H$_3$ (**3**), Chart 1] exhibited high catalytic activities in ethylene polymerization,[7] and the activity of **2** in the presence of Et$_2$AlCl was higher than that in the presence of MAO.[7b] We also demonstrated that the choice of aluminum promoters directly controls olefin coordination insertion or metathesis pathway exclusively: the effective catalyst (**2**−AlMe$_3$) for the ring-opening metathesis polymerization of norbornene can be tuned to being an effective catalyst for ethylene polymerization only by replacement of the Al cocatalyst (Et$_2$AlCl) employed.[7b] Since catalyst **1** did not show any catalytic activity for styrene polymerization and also since the resultant polymer by attempted ethylene/styrene copolymerization afforded polyethylene,[7d] we decided to clarify the scope and limitation of these vanadium catalyst systems based on both arylimido and aryloxo ligands. In particular, we focused on copolymerization of ethylene with cyclic olefins, because various examples were known concerning copolymerization of ethylene with bicyclic and multicyclic olefins using the classical Ziegler type catalyst systems consisting of VOCl$_3$, VCl$_2$(OEt), and Et$_3$Al$_2$Cl$_3$.[8] This is also because that some cyclic olefin copolymers are known to be amorphous materials with a promising combination of high transparency in the UV−vis region along with humidity- and heat-resistance.[9,10] In this paper, we wish to demonstrate that these vanadium catalysts (**1**−**3**) are

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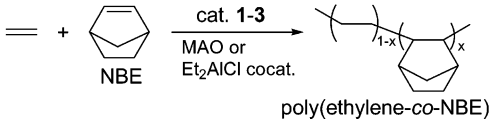
Scheme 1



especially effective for copolymerization of ethylene with norbornene, affording a high molecular weight copolymer with narrow molecular weight distributions (Scheme 1). We would also like to show that (1) the effects of Al cocatalyst (MAO or Et_2AlCl) toward the catalytic activity, the NBE incorporation, the M_n value etc. were highly dominant over the effect of the aryloxide ligand employed, (2) and a significant effect of comonomer toward both the catalytic activity and the comonomer incorporation was observed in the ethylene copolymerizations in this paper.

Results and Discussion

1. Ethylene Polymerization Catalyzed by $VCl_2(N-2,6-Me_2C_6H_3)(OAr)$ (1—3)—MAO, Et_2AlCl Catalyst Systems. Ethylene polymerizations by **1**, **2** and **3** were conducted in toluene using a 100 mL scale autoclave in the presence of MAO white solid [prepared by removing toluene and an excess amount of $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.)] or Et_2AlCl (1.00 mol/L *n*-hexane solution, Kanto Chemical Co., Inc.) as the cocatalyst. The results are summarized in Table 1.

Complexes **1**−**3** showed high catalytic activities for ethylene polymerization in the presence of MAO, as communicated previously.[7c] The observed activity with **1** was higher than those with **2** and **3**, and the activity seemed to be increasing at low catalyst concentration (runs 4−5). These results suggest that the ortho substituents on the aryloxide ligand affect the catalytic activity. The resultant polymers were linear polyethylene confirmed by ^{13}C NMR spectra,[7c] and the M_n values were relatively high with unimodal molecular weight distributions [$M_w = (1.03-1.27) \times 10^6$, $M_n = (2.38-2.73) \times 10^5$, $M_w/M_n = 3.89-4.92$], although the M_w/M_n value of **2** (run 2) was somewhat larger than that previously reported ($M_w = 2.03 \times 10^6$, $M_n = 7.44 \times 10^5$, $M_w/M_n = 2.73$, **2** 5.0 μmol, Al/V = 1000, 25 °C, 10 min).[7b] Although it is not clear why the distribution was rather broad, one probable reason could be the result of polyethylene precipitation during the polymerization under these conditions. In fact, under the optimized conditions, polyethylene possessing higher M_n values with the narrow distributions could be obtained by using the **1**−MAO catalyst system [$M_n = (1.67-1.75) \times 10^6$, $M_w/M_n = 1.64-1.71$, runs 4−5].

Notable enhancement in the catalytic activity using **1**−**3** was observed when Et_2AlCl was used in place of MAO at 0 °C, and the activity seemed to be increasing in the following order: **3** (13700 kg of PE/(mol-V·h), run 8) > **1** (11700, run 6) > **2** (9490, run 7) under the same conditions (complex 0.05 μmol, Al/V = 5000, ethylene 8 atm). Resultant polymers (PEs) possessed high molecular weights with narrow molecular weight distributions [$M_n = (1.12-2.57) \times 10^6$, $M_w/M_n = 1.42-2.21$]. The unimodal distributions for resultant PEs (prepared in the presence of MAO or Et_2AlCl cocatalyst) suggest that these polymerizations took place with single catalytically active species. The observed difference in both the activities and M_n values for resultant PE between MAO and Et_2AlCl cocatalyst might be due to the fact that different catalytically active species (effect of ion pairing[11]) were present in these polymerizations. In particular, the resultant PE prepared by **1** (run 6) possessed a very high molecular weight ($M_n = 2.57 \times 10^6$) with low PDI value ($M_w/M_n = 1.42$), suggesting the possibility of living polymerization in this catalysis.

Table 2 summarizes the results for ethylene polymerization by the **1**−Et_2AlCl catalyst under various conditions. The observed activity of **1** was not dependent upon the catalyst concentration employed but was dependent upon ethylene pressure, because relatively good first-order linearity between the activity and ethylene pressure was observed (Figure 1). The resultant PEs possessed high molecular weights, and the M_n values were not affected by varying the catalyst concentration. Note that a first order relationship between TON values [yields, molar amount of ethylene consumed/(mol-V)], and M_n values with narrow M_w/M_n values could be observed (Figure 2), although the M_n value for resultant PEs were very high ($1.43-2.63 \times 10^6$). These results suggest that this polymerization proceeds in a quasi living manner.[12]

2. Effect of Al Cocatalyst (MAO or Et_2AlCl) in Ethylene/Norbornene (NBE) Copolymerization Catalyzed by $VCl_2(N-2,6-Me_2C_6H_3)(O-2,6-Me_2C_6H_3)$ (1). We already reported that the isopropyl analogue **2** exhibited low catalytic activities for both propylene and 1-hexene polymerizations (affording irregular and atactic polymer, respectively).[7b] Although the results suggest that these complexes may not be suited as a catalyst precursor for the ethylene copolymerizations, we explored a possibility for copolymerization of ethylene with norbornene (NBE) using **1** as the catalyst precursor in the presence of MAO, Et_2AlCl cocatalyst.[13]

2.1. Ethylene/NBE Copolymerization with the 1—MAO Catalyst System. As shown in Table 3, the **1**−MAO catalyst system exhibited both high catalytic activity and efficient NBE incorporation. The resultant

Table 1. Effect of Cocatalyst (MAO or Et_2AlCl) in Ethylene Polymerization Catalyzed by $VCl_2(N-2,6-Me_2C_6H_3)(OAr)$ [Ar = $2,6-Me_2C_6H_3$ (1), $2,6-{}^iPr_2C_6H_3$ (2), $2,6-Ph_2C_6H_3$ (3)][a]

run no.	catal (μmol)	Al cocatal	temp/°C	polymer yield/ mg	activity[b]	M_n[c] $\times 10^{-5}$	M_w/M_n[c]
1	**1** (2.5)	MAO	25	737	1770	2.73	4.65
2	**2** (2.5)	MAO	25	439	1050	2.38	4.92
3	**3** (2.5)	MAO	25	453	1090	2.65	3.89
4	**1** (1.0)	MAO	25	488	2930	17.5	1.64
5	**1** (1.0)	MAO	25	467	2800	16.7	1.71
6	**1** (0.05)	Et_2AlCl	0	97	11 700	25.7	1.42
7	**2** (0.05)	Et_2AlCl	0	79	9490	11.2	1.92
8	**3** (0.05)	Et_2AlCl	0	115	13 700	15.8	2.21

[a] Conditions: toluene 30 mL, Et_2AlCl 250 μmol or MAO 2.5 mmol, ethylene 8 atm, 10 min. [b] Activity in kg of polymer/(mol-V·h). [c] GPC data in *o*-dichlorobenzene vs polystyrene standards.

Table 2. Effect of Ethylene Pressure in Ethylene Polymerization by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (1)−Et_2AlCl Catalyst System[a]

run no.	**1** (μmol)	ethylene/ atm	polymer yield/mg	activity[b]	TON[c]	$M_n{}^d \times 10^{-5}$	$M_w/M_n{}^d$
9	**1** (0.025)	8	46	11100	65600	26.3	1.35
6	**1** (0.05)	8	97	11700	69200	25.7	1.42
10	**1** (0.05)	6	77	9240	54900	19.3	1.56
11	**1** (0.05)	4	24	2880	17100	14.5	1.58
12	**1** (0.10)	8	189	11400	67400	23.1	1.50
13	**1** (0.10)	6	142	8540	50600	18.6	1.52
14	**1** (0.10)	4	76	4580	27100	14.3	1.61

[a] Conditions: toluene 30 mL, Et_2AlCl 250 μmol, 0 °C, 10 min. [b] Activity in kg of PE/(mol-V·h). [c] TON (turnover numbers) = ethylene consumed (mmol)/ vanadium (mmol). [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

Table 3. Copolymerization of ethylene with norbornene (NBE) by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (1) - MAO catalyst system[a]

run no.	catal (μmol)	MAO Al/V[b] × 10^{-3}	ethylene/ atm	NBE concn[c]/(mol/L)	polymer yield/mg	activity[d]	NBE content[e]/mol %	$M_n{}^f \times 10^{-5}$	$M_w/M_n{}^f$
4	**1** (1.0)	2.5	8		488	2930		17.5	1.64
15	**1** (1.0)	1.0	8	0.30	254	1520	16.5	7.57	1.89
16	**1** (1.0)	2.0	8	0.30	277	1660		7.58	1.77
17	**1** (1.0)	2.5	8	0.30	260	1560	15.9	7.78	1.85
18	**1** (1.0)	3.0	8	0.30	259	1560		7.22	1.85
19	**1** (1.0)	2.5	8	0.10	365	2190	6.9	11.3	1.70
20	**1** (0.3)	8.3	8	0.10	151	3010	8.9	7.57	1.97
21	**1** (1.0)	2.5	8	0.20	285	1710	13.4	8.74	1.77
22	**1** (0.5)	5.0	8	0.20	208	2490	13.2	6.43	1.97
17	**1** (1.0)	2.5	8	0.30	260	1560	15.9	7.78	1.85
23	**1** (1.0)	2.5	8	0.30	263	1580			
24	**1** (1.0)	2.5	8	0.40	213	1280	19.2	7.30	1.99
25	**1** (1.0)	2.5	8	0.50	146	875	23.9	2.99	1.79
26	**Ind-Ti**[g] (0.2)	15.0	4	0.50	241	7220	25.6	9.15	1.72
27[h]	**1** (1.0)	2.5	8	0.50	90	540	18.8	4.48	1.55
28	**1** (1.0)	2.5	8	0.80	72	434		1.33	1.83
29	**1** (1.0)	5.0	8	0.80	88	527		1.55	2.08
30	**1** (2.5)	1.0	8	0.80	182	437	29.2	1.11	1.83
31	**1** (2.5)	1.0	8	1.00	153	367	32.9	1.10	1.85
32	**1** (2.5)	1.0	8	1.00	147	353			
33	**1** (5.0)	0.50	8	2.00	160	192	38.3	0.448	1.89
34	**1** (5.0)	0.50	8	3.00	136	163	45.3	0.363	1.93

[a] Conditions: toluene 30 mL, MAO 2.5 mmol (prepared by removing $AlMe_3$ and toluene from PMAO), ethylene 8 atm, 25 °C, 10 min. [b] Molar ratio of Al/V. [c] Norbornene (NBE) concentration charged (mol/L). [d] Activity in kg of polymer/(mol-M·h) (M = Ti or V). [e] NBE content (mol %) estimated by ^{13}C NMR spectra. [f] GPC data in *o*-dichlorobenzene vs polystyrene standards. [g] The copolymerization using (indenyl)$TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$−MAO catalyst (ethylene 4 atm, 25 °C, 10 min) cited from ref 16b. [h] Polymerization at 0 °C.

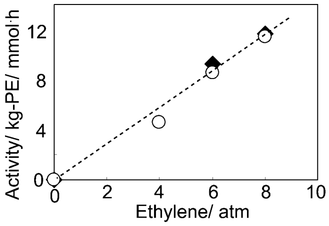


Figure 1. Ethylene pressure dependence toward the catalytic activity in ethylene polymerization by the **1**−Et_2AlCl catalyst system. Complex **1**: 0.05 μmol (◆, runs 6,10), 0.10 μmol (○, runs 12−14).

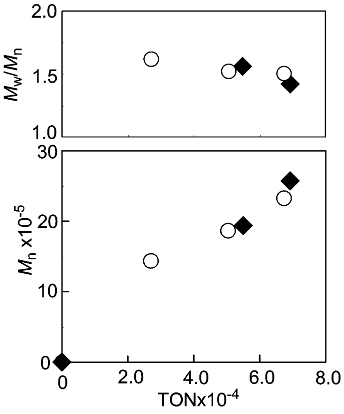


Figure 2. Plots of M_n and M_w/M_n vs TON [turnover number: molar amount of ethylene consumed/(mol-V)]. Complex **1**: 0.05 μmol (◆, runs 6,10), 0.10 μmol (○, runs 12−14).

poly(ethylene-*co*-NBE)s possessed relatively high molecular weights with unimodal molecular weight distributions [$M_n = (3.63−113) \times 10^4$, $M_w/M_n = 1.70−2.08$]. The NBE content increased upon increasing the initial NBE concentrations, and the M_n value decreased upon increasing the NBE content estimated by ^{13}C NMR spectra established in the previous reports (Ti, Zr),[14−16] especially by Tritto et al.[15] The NBE incorporation by **1** seems more efficient than that by (indenyl)$TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ which exhibits the efficient NBE incorporation in this copolymerization,[16] because the NBE content using **1** with ethylene at 8 atm (23.9 mol %, run 25) was the same as that using the indenyl−aryloxy titanium complex (NBE 25.6 mol %, run 26) with ethylene at 4 atm under the same initial NBE concentrations (NBE 0.50 mol/L). However, the activity by **1** was somewhat low under the same conditions [7220 kg of polymer/(mol-Ti·h) vs 875 kg of polymer/(mol-V·h)]. The activity for **1** decreased at the lower temperature of 0 °C, as observed in the ethylene homopolymerization.[7c]

It is interesting to note that high catalytic activity was observed even at a lower Al/V molar ratio (run 15),

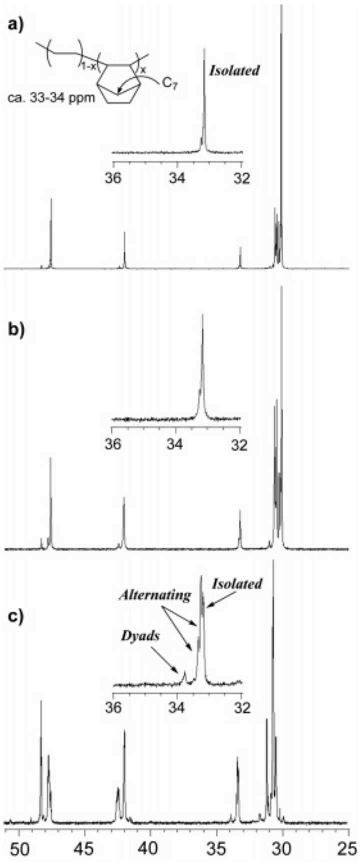
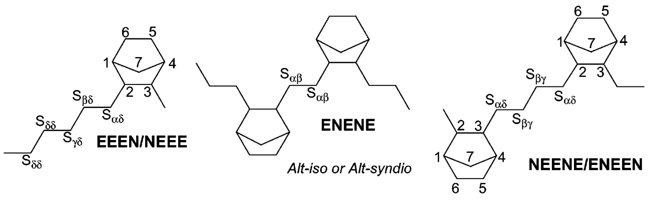


Figure 3. ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) prepared by the **1**−MAO catalyst system: (a) NBE 15.9 mol % (run 17); (b) NBE 29.2 mol % (run 30); (c) NBE 38.3 mol % (run 33).

Scheme 2



and the ratio did not affect strong influences toward the activity as well as the NBE content in the copolymer (runs 15−18, Al/V molar ratio = 1000−3000). The M_n values were unchanged under these conditions. The fact that a relatively excess amount of MAO was not necessary for exhibiting the high catalytic activity was somewhat similar to what was observed in ethylene polymerization.[7c] Moreover, the fact that the M_n values were independent of the Al/V molar ratios suggests that the dominant chain transfer in this copolymerization was not chain transfer to Al from the vanadium−alkyl species.

Figure 3 shows the typical ^{13}C NMR spectra of poly(ethylene-*co*-NBE)s prepared by the **1**−MAO catalyst system (NBE content 15.9−38.3 mol %),[13] and the possible sequences in the copolymer are depicted in Scheme 2. It is clear that NBE was incorporated as isolated or alternating manner (Figure 3a−c) with a mixture of iso- and syndiotactic NBE configurations,[15,16] and a small amount of NBE repeating unit (NN dyad) was also observed for the copolymer with high NBE content (run 33, Figure 3c). These results clearly indicate that synthesis of the copolymer with higher NBE content (with random incorporation consisting of a mixture of isolated, alternating, and repeating NBE units) seems to be difficult in this catalysis.

2.2. Ethylene/NBE Copolymerization Catalyzed by the 1—Et$_2$AlCl System. Since a significant effect of cocatalyst (MAO or Et$_2$AlCl) toward the catalytic activity for ethylene polymerization was observed (Table 1), copolymerizations of ethylene with NBE by **1**−Et$_2$AlCl were thus explored. The results under various conditions are summarized in Table 4.[13]

The copolymerizations took place with remarkable catalytic activities [22300−30600 kg of polymer/(mol-V·h), runs 35−37], and the observed activities were higher than that in ethylene homopolymerization [11700 kg of PE/(mol-V·h), run 6]. The catalytic activity at 25 °C was significantly lower than that at 0 °C (runs 43−45), and the NBE content increased due to the increase in the initial NBE/ethylene molar ratio in the polymerization solution. The resultant polymers were poly(ethylene-*co*-NBE)s and possessed extra high molecular weights with unimodal molecular weight distributions. Both the activity and the M_n value were dependent upon the Al/V molar ratio employed (runs 35−38), but the NBE content was not affected by the Al/V molar ratio (runs 36−37). NBE was efficiently incorporated into the polymer chain, and the content increased upon increasing the NBE initial concentration. Note that the NBE incorporation by **1**−Et$_2$AlCl was less efficient than that by the **1**−MAO catalyst system [for example, at the same NBE initial concentration, [NBE] = 0.3 mol/L, NBE content 15.9 mol % (run 17, MAO cocatalyst) vs 5.9 mol % (run 41, Et$_2$AlCl cocatalyst); [NBE] = 1.00 mol/L, NBE content 32.9 mol % (run 31) vs 17.3 mol % (run 47)], although the M_n values for the copolymers prepared by **1**−Et$_2$AlCl were much higher than those prepared by **1**−MAO catalyst. This should be a unique characteristic in that *the nature of Al cocatalyst directly affects both the NBE incorporation and the molecular weight* in the copolymerization.

It should be noted that *both the activity and the M_n values were unchanged upon increasing the NBE concentration* [runs 36, 40−43, 46−48; activity 23000−31700 kg of polymer/(mol-V·h), $M_n = (2.12−2.70) \times 10^6$, $M_w/M_n = 1.29−1.53$] under certain NBE concentration conditions (initial NBE concentration 0.20−1.00 mol/L). Moreover, the resultant copolymers in certain experimental runs possessed narrow molecular weight distributions (run 40, $M_w/M_n = 1.33$; run 42, $M_w/M_n = 1.29$), which may suggest the possibility of a living polymerization.[17] Since it has been generally known that both the activity and the M_n value are dependent upon the NBE contents in the copolymerizations by ordinary metallocenes or half-titanocenes[14−16] as can be seen in the copolymerization by the **1**−MAO catalyst system, a distinct difference using this catalyst system in the copolymerization can be thus observed. In contrast, the dominant chain transfer in the copolymerization would be the alkyl transfer in this catalysis, because the M_n values were affected by the Al/V molar ratios; this fact is in unique contrast to that observed in the copolymerization by the **1**−MAO catalyst system, in which the M_n values were independent of the Al/V molar ratios but dependent upon the NBE contents. These clearly indicate that the nature of Al cocatalyst *directly* affects the copolymerization behavior (the NBE incorporation, dependence on the M_n values, dominant chain transfer) in this catalysis.

Table 4. Copolymerization of Ethylene with NBE by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (1)−Et_2AlCl Catalyst System[a]

run no.	catal **1**/μmol	Et_2AlCl Al/V[b] × 10^{-2}	ethylene/atm	NBE concn[c]/(mol/L)	polymer yield/mg	activity[d]	NBE content[e]/mol%	M_n[f] × 10^{-5}	M_w/M_n[f]
6	0.05	50.0	8		97	11700		25.7	1.42
35	0.05	20.0	8	0.40	215	25800		22.5	1.61
36	0.05	50.0	8	0.40	255	30600	10.2	21.2	1.50
37	0.05	100	8	0.40	186	22300	10.8	16.2	1.72
38	0.05	200	8	0.40	70	8400		10.8	1.89
39	0.05	50.0	8	0.10	151	18200	4.6	24.6	1.45
40	0.05	50.0	8	0.20	215	25800	5.1	27.0	1.33
41	0.05	50.0	8	0.30	232	27800	5.9	22.8	1.50
36	0.05	50.0	8	0.40	255	30600	10.2	21.2	1.50
42	0.05	50.0	8	0.50	265	31700	10.4	25.4	1.29
43	0.05	50.0	8	0.50	258	31000			
44[g]	0.05	50.0	8	0.50	12	1400			
45[g]	1.0	2.50	8	0.50	181	1090	17.9	8.61	1.59
46	0.05	50.0	8	0.80	244	29200	15.4	25.5	1.39
47	0.05	50.0	8	1.00	200	24000	17.3	22.9	1.53
48	0.05	50.0	8	1.00	192	23000			
49	1.0	2.50	8	1.50	383	2290	26.0	11.7	1.72
50	1.0	2.50	8	2.00	407	2440	31.0	12.8	1.49
51	1.0	2.50	8	3.00	285	1710	31.5	10.2	1.89
52	1.0	2.50	8	4.00	137	824	31.3	10.7	1.85
53	1.0	2.50	8	4.00	132	792			
54	2.0	1.25	4	4.00	205	615	39.9	3.27	1.73
55	2.0	1.25	2	4.00	102	306	44.4	1.30	1.95
56	5.0	0.50	2	10.0	54	65	45.7	0.905	2.20

[a] Conditions: toluene 30 mL, Et_2AlCl 250 μmol (run 35 100 μmol, run 37 500 μmol, run 38 1.0mmol), 0 °C, 10 min. [b] Molar ratio of Al/V. [c] Norbornene (NBE) concentration charged (mol/L). [d] Activity in kg of polymer/(mol-V·h). [e] NBE content (mol %) estimated by ^{13}C NMR spectra. [f] GPC data in *o*-dichlorobenzene vs polystyrene standards. [g] Polymerization at 25 °C.

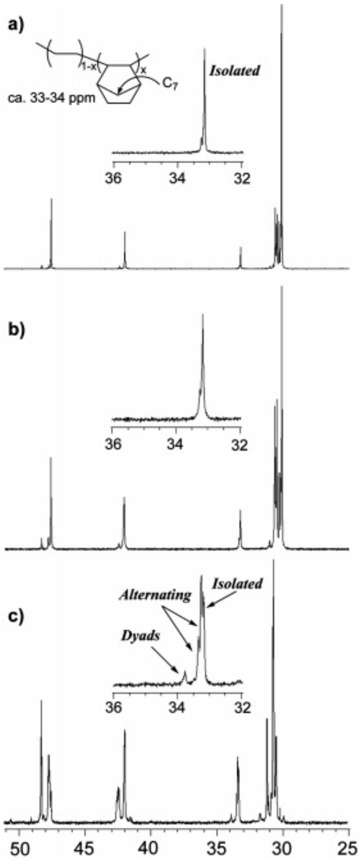


Figure 4. ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) prepared by the **1**−Et_2AlCl catalyst system: (a) NBE 10.2 mol % (run 36); (b) NBE 17.3 mol % (run 47); (c) NBE 44.4 mol % (run 55).

Figure 4 shows typical ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s prepared by a **1**−Et_2AlCl catalyst system (NBE content 10.2−44.4 mol %). Although a significant difference in the NBE incorporation was observed in the copolymerization between **1**−MAO and **1**−Et_2AlCl catalyst systems, no distinct differences were observed in the microstructures for the resultant copolymers: NBE was incorporated as isolated or in an alternating manner (Figure 4a−c), and a small amount of NBE repeating unit (NN dyad) was also observed for the polymer with high NBE content (run 55, Figure 4c).

Although the observed activity was independent of the NBE concentration under certain low NBE concentration regions (runs 36, 40−43, 46−48, NBE 0.20−1.00 mol/L), the activity decreased under higher NBE concentration conditions (runs 49−53) at lower ethylene pressure (runs 54−56). The M_n values also decreased upon increasing the NBE content under these high NBE concentration conditions. As shown in Figure 4c, resonances ascribed to the NBE repeating units in addition to the isolated and alternating NBE incorporated sequences were observed in the copolymer with high NBE content (44.4 mol %), but the percentage was very low (less than 7% based on the integration ratio). Therefore, it seems difficult to prepare the copolymer with an NBE content higher than 50 mol % in this catalytic copolymerization.

3. Effect of Aryloxo Ligand in Ethylene/NBE Copolymerization Catalyzed by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ (1—3)—Et_2AlCl, MAO Catalyst Systems. As described above, the nature of the Al cocatalyst directly affected the catalytic activity, the NBE incorporation, the molecular weight of the resultant copolymer and the dominant chain-transfer pathway in the copolymerization catalyzed by **1**. Since both the activity and the NBE incorporation should be affected by the anionic donor ligand employed, as could be seen in the copolymerization of ethylene with cyclohexene by (aryloxo)(cylopentadienyl)titanium complex−MAO catalyst systems,[18] the ethylene/NBE copolymerizations with (arylimido)vanadium(V) complexes containing various aryloxo ligands were thus explored. The results are summarized in Table 5.

Table 5. Copolymerization of Ethylene with Norbornene (NBE) by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ [Ar = $2,6\text{-}Me_2C_6H_3$(1), $2,6\text{-}iPr_2C_6H_3$(2), $2,6\text{-}Ph_2C_6H_3$(3)] - cocatalyst systems[a]

run no.	complex (μmol)	Al cocatal (Al/V × 10^{-3})[b]	temp/°C	NBE conc[c]/mol %	polymer yield/mg	activity[d]	NBE content[e] mol/L	M_n[f] × 10^{-5}	M_w/M_n[f]
6	**1** (0.05)	Et_2AlCl (5.0)	0		97	11700		25.7	1.42
42	**1** (0.05)	Et_2AlCl (5.0)	0	0.50	265	31700	10.4	25.4	1.29
47	**1** (0.05)	Et_2AlCl (5.0)	0	1.00	200	24000	17.3	22.9	1.53
7	**2** (0.05)	Et_2AlCl (5.0)	0		79	9490		11.2	1.92
57	**2** (0.05)	Et_2AlCl (5.0)	0	0.50	169	20300	10.2	10.4	2.05
58	**2** (0.05)	Et_2AlCl (5.0)	0	1.00	199	23900	15.5	16.1	1.54
8	**3** (0.05)	Et_2AlCl (5.0)	0		115	13700		15.8	2.21
59	**3** (0.05)	Et_2AlCl (5.0)	0	0.50	125	15000	9.9	9.09	2.00
60	**3** (0.05)	Et_2AlCl (5.0)	0	1.00	140	16700	14.5	10.7	1.89
4	**1** (1.0)	MAO (2.5)	25		488	2930		17.5	1.64
25	**1** (1.0)	MAO (2.5)	25	0.50	146	875	23.9	2.99	1.79
31	**1** (2.5)	MAO (1.0)	25	1.00	153	367	32.9	1.10	1.85
2	**2** (2.5)	MAO (1.0)	25		439	1050		2.38	4.92
61	**2** (2.5)	MAO (1.0)	25	0.50	136	326	26.4	0.803	2.13
62	**2** (2.5)	MAO (1.0)	25	1.00	72	173	31.3	0.598	2.27
3	**3** (2.5)	MAO (1.0)	25		453	1090		2.65	3.89
63	**3** (2.5)	MAO (1.0)	25	0.50	222	532	24.7	0.439	2.68
64	**3** (2.5)	MAO (1.0)	25	1.00	65	156	33.6	0.387	2.10

[a] Conditions: toluene 30 mL, Et_2AlCl 250 μmol or MAO 2.5 mmol, ethylene 8 atm, 0 °C for Et_2AlCl runs and 25 °C for MAO runs, 10 min. [b] Molar ratio of Al/V. [c] Norbornene (NBE) concentration charged (mol/L). [d] Activity in kg of polymer/(mol-V·h). [e] NBE content (mol %) estimated by ^{13}C NMR spectra. [f] GPC data in *o*-dichlorobenzene. vs polystyrene standards.

The catalytic activity in the copolymerization by (**1**−**3**)−Et_2AlCl catalyst system increased in the following order (NBE 1.00 mol/L): **1** [24000 kg of polymer/(mol-V·h), run 47], **2** (23900, run 58) > **3** (16700, run 60). The M_n value for resultant copolymer increased in the following order: **1** > **2**, **3**. The results suggest that the nature of the aryloxo ligand affects both the catalytic activity and the M_n value. However, no distinct differences in the NBE contents in the copolymers were observed under the same conditions.

The activity in the ethylene/NBE copolymerization by (**1**−**3**)−MAO catalyst systems also increased in the following order (NBE 1.00 mol/L): **1** [367 kg of polymer/(mol-V·h), run 31] > **2** (173, run 62), **3** (156, run 64). The M_n value for the resultant copolymer increased in the following order: **1** > **2** > **3**. The results also suggest that the aryloxo ligand affects both the catalytic activity and the M_n value. However, as seen in the copolymerization in the presence of Et_2AlCl, no distinct differences in the NBE contents were observed. Note that the Et_2AlCl cocatalyst systems showed higher catalytic activities than the MAO cocatalyst systems, affording the copolymers with higher M_n values in all cases, whereas the MAO cocatalyst systems showed more efficient NBE incorporation than the Et_2AlCl cocatalyst systems. In contrast, as shown in Figure 5, no significant differences were observed in the microstructure by ^{13}C NMR spectra for the resultant copolymers prepared by (**1**−**3**)−cocatalyst systems: NBE was incorporated as isolated or alternating, and a trace amount of NBE repeating unit (NN dyad) was also observed for the polymer with higher NBE content (Figure 5b,c). These results also indicate that both the monomer reactivity and monomer sequence can only be drastically tuned not by the modification of the aryloxo ligand but by the nature of cocatalyst (MAO or Et_2AlCl) employed.

Since the observed effect of Al cocatalyst especially toward both the catalytic activity and the NBE incorporation (the M_n values) is more significant than that by the aryloxo ligand, we believe, the observed facts are unique characteristic for using this vanadium catalyst in olefin polymerization, in which *the nature of the cocatalyst directly controls* the catalytic activity, the NBE incorporation, and the dominant chain transfer pathway.

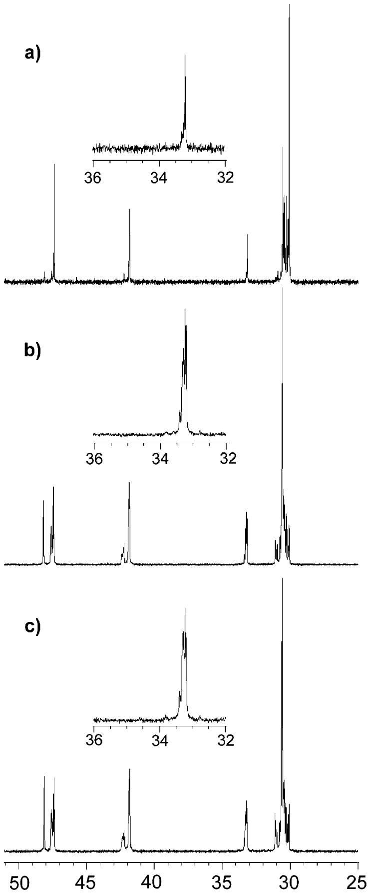


Figure 5. ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) prepared by (**1**−**3**)−cocatalyst (Et_2AlCl or MAO) catalyst systems: (a) NBE 14.5 mol % (by **3**−Et_2AlCl catalyst, run 60); (b) NBE 31.3 mol % (by **2**−MAO catalyst, run 62); (c) NBE 33.6 mol % (by **3**−MAO catalyst, run 64).

4. Attempts at Copolymerization of Ethylene with 1-Hexene (Hex), with Cyclopentene (CPE), or with Styrene by 1—Cocatalyst (Et_2AlCl, MAO) Catalyst Systems. Since **1** exhibited unique characteristics in the ethylene/NBE copolymerization, as described above, the copolymerizations of ethylene with

Table 6. Copolymerization of Ethylene with 1-Hexene (Hex), Cyclopentene (CPE), Styrene by 1−Cocatalyst System[a]

run no.	catal (μmol)	Al cocatal (Al/V$\times10^{-3}$)[b]	polymer yield/mg	comonomer[c] (mol/L)	activity[d]	comonomer content[e]/mol%	$M_n{}^f \times 10^{-5}$	$M_w/M_n{}^f$
6	**1** (0.05)	Et_2AlCl (5.0)		97	11700		25.7	1.42
65	**1** (0.05)	Et_2AlCl (5.0)	Hex (0.27)	145	17400	n.d.[g]	9.63	1.92
66	**1** (0.05)	Et_2AlCl (5.0)	Hex (1.33)	104	12400	0.8	8.75	1.90
67	**1** (0.05)	Et_2AlCl (5.0)	Hex (2.67)	49	5830		4.97	2.19
42	**1** (0.05)	Et_2AlCl (5.0)	NBE (0.50)	265	31700	10.4	25.4	1.29
25	**1** (1.0)	MAO (2.5)	NBE (0.50)	146	875	23.9	2.99	1.79
68	**1** (5.0)	MAO (0.50)	CPE (0.50)	260	312	n.d.[g]	1.83	1.89
69	**1** (10.0)	MAO (0.50)	styrene (0.73)[h]	75.2	15.0	n.d.[g]	1.77	1.65
70	**1** (10.0)	MAO (0.50)	styrene (1.45)[h]	52.4	10.5	n.d.[g]	0.541	1.23[i]

[a] Conditions: toluene + comonomer = 30 mL, ethylene 8 atm, Et_2AlCl 250 μmol or MAO 2.5 mmol, 0 °C for polymerization by Et_2AlCl and 25 °C for those by MAO, 10 min. [b] Molar ratio of Al/V. [c] Comonomer charged (mol/L). [d] Activity in kg of polymer/(mol-V·h). [e] Comonomer content (mol %) estimated by ^{13}C NMR spectra. [f] GPC data in *o*-dichlorobenzene vs polystyrene standards. [g] No detectable comonomer incorporations confirmed by ^{13}C−NMR spectra. [h] Attempted copolymerization results for 30 min cited from ref 7d (MAO 5.0 mmol). [i] Trace amount of low MW shoulder ($M_n = 2900$, $M_w/M_n = 1.65$) was observed in the GPC trace.

other olefins such as 1-hexene, cyclopentene (CPE), and styrene were explored under similar conditions. The results are summarized in Table 6.

Although the **1**−Et_2AlCl catalyst exhibited remarkable catalytic activity and rather efficient comonomer incorporation in ethylene/NBE copolymerization, poor 1-hexene incorporation (0.8 mol %, run 66) was observed in the ethylene/1-hexene copolymerization. The activity initially increased upon the presence of 1-hexene (runs 65−66), and the resultant polymer possessed relatively high molecular weight with unimodal molecular weight distributions. Both the activity and the M_n value decreased under higher 1-hexene concentrations. The observed facts may be related to the extremely lower activity in the 1-hexene homopolymerization (2.03 kg of PH/(mol-V·h), in 1-hexene at 25 °C, MAO cocatalyst, Al/V = 500) and/or in the propylene polymerization by **2** [4.02 kg of PP/(mol-V·h), MAO cocatalyst, Al/V = 1000, in toluene at propylene 4 atm, 25 °C, 1 h][7b] than that in the ethylene polymerization by **2** − MAO catalyst [run 2, 1050 kg of PE/(mol-V·h), 131 kg of PE/(mol-V·h·atm)], strongly suggesting that a steric bulk of the substituent in α-olefin (H vs *n*-butyl) affects the activity, probably due to the fact that the polymerization took place with a 2,1-insertion mode in this catalysis.

The attempted copolymerization of ethylene with CPE afforded a polymer containing a trace amount of CPE, clearly suggesting that the coordination/insertion of CPE seems to be difficult in this catalysis due to the increased steric bulk (compared to NBE) as can be seen in the above copolymerization. In addition, attempted copolymerization of ethylene with styrene afforded linear polyethylene, and the activity drastically decreased upon the presence of styrene.[7d] Since a drastic effect toward both the activity and the comonomer incorporation was observed in this catalysis, it is thus concluded that the copolymerizations catalyzed by (arylimido)(aryloxo)vanadium complexes were strongly affected not only by the Al cocatalyst but also by the comonomer employed.

Concluding Remarks

We have shown that (arylimido)(aryloxo)vanadium complexes of the type $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ (**1**−**3**) exhibit remarkable catalytic activities for both ethylene homopolymerization and ethylene/norbornene (NBE) copolymerization in the presence of Al cocatalyst. In particular, the **1**−Et_2AlCl catalyst exhibited notable catalytic activities for the copolymerizations, affording ultrahigh molecular weight poly(ethylene-*co*-NBE)s with unimodal, narrow molecular weight distributions. The contents in this paper can be summarized as follows.

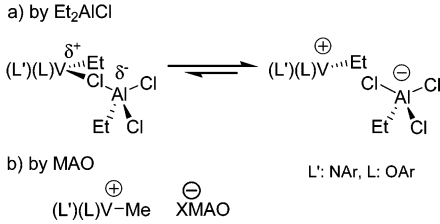
(1) The notable effect of Al cocatalyst (MAO, Et_2AlCl) toward the catalytic activities, the NBE incorporation, and the M_n values for resultant copolymer was demonstrated in the copolymerization with **1**−cocatalyst systems. The catalytic activities by Et_2AlCl were much higher than those by MAO, and the M_n values for the resultant copolymer prepared in the presence of Et_2AlCl were much higher than for those prepared in the presence of MAO. The M_n values were not dependent upon the NBE contents in the copolymers but dependent upon the Al/V molar ratios when the copolymerizations were employed in the presence of Et_2AlCl; the M_n values were not dependent upon the Al/V molar ratios but dependent upon the NBE contents in the copolymers when the copolymerizations were performed in the presence of MAO.

(2) The aryloxide ligand affects the catalytic activity in both ethylene polymerization and ethylene/NBE copolymerization, but notable differences toward the NBE incorporation, microstructures, and the M_n values for resultant copolymers were not observed. Since the effect was not so significant as that by Al cocatalyst employed, unique characteristics for using this catalyst have been demonstrated.

(3) The effect of the comonomer employed strongly affects both the catalytic activity and the comonomer incorporation. The attempted ethylene/cyclopentene (CPE) copolymerization under the same conditions for the ethylene/NBE copolymerization, afforded polymers with a trace amount of CPE incorporation. The attempted copolymerization of ethylene with styrene afforded polyethylene and the activity decreased upon the presence of styrene. Moreover, the poor 1-hexene incorporation was observed in the ethylene/1-hexene copolymerization by the **1**−Et_2AlCl catalyst system. These results are thus in unique contrast to the facts observed in the ethylene/NBE copolymerization.

The noble cocatalyst effect was observed between MAO and Et_2AlCl for both the ethylene polymerization and the ethylene/NBE copolymerization, although both catalyst systems offered copolymers with unimodal molecular weight distributions, strongly suggesting that these copolymerizations took place with single catalytically active species. In addition, the above-mentioned differences may clearly imply that the active species, in other word, the nature of ion pairing species[11,19] formed by these two cocatalyst systems were different. The probable, plausible reason for the observed differ-

Scheme 3. Assumed Catalytically Active Species



ence may be thus due to the different catalytically active species, giving the catalyst/cocatalyst nuclearity effect[19] generated in the two systems as exemplified in Scheme 3. Since the cationic vanadium−alkyl species formed by the precursor complex and Et_2AlCl may not be stable and thus stay in an equilibrium between chloro-bridged and cationic alkyl species due to the less steric bulk and stronger nucleophilic nature of Et_2AlCl, an isolated cationic species would be formed when MAO was employed as the cocatalyst. The equilibrium by Et_2AlCl would stabilize the catalytically active species, leading to the higher catalytic activity: the equilibrium may not be suited for coordination of the bulky monomer, leading to a less efficient NBE incorporation than that by MAO in the copolymerization.[20] Since the bridged aluminum compound would present itself relatively close to the active center, the dominant chain transfer would be the transfer to aluminum alkyls, whereas the dominant chain transfer would be β-H elimination in the copolymerization in the presence of MAO cocatalyst. The results presented here would be helpful for understanding the coordination polymerization mechanism as well as for designing novel catalysts for precise olefin polymerization using the so-called post-metallocene type transition metal catalysts based on vanadium(V) complexes.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox, and was used without further purification. Norbornene of reagent grade (Aldrich) was stored in the drybox, and was used without further purification. Syntheses of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ (**1**, Ar = 2,6-$Me_2C_6H_3$; **2**, Ar = 2,6-$^iPr_2C_6H_3$; **3**, Ar = 2,6-$Ph_2C_6H_3$) were according to the previous reports.[7] Et_2AlCl solution in *n*-hexane (1.0 mol/L) was purchased from Kanto Co. and was used as received. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 °C for removing toluene and $AlMe_3$ and then heated at >100 °C for 1 h for completion) in the drybox to give white solids.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H). All deuterated NMR solvents were stored over molecular sieves under nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me_4Si. ^{13}C NMR spectra for polyethylene and poly(ethylene-*co*-NBE)s were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 6000−7000. The analysis samples of copolymers were prepared by dissolving polymer in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt) and the spectrum was measured at 110 °C. The NBE contents and the monomer sequence distributions in the resultant copolymers were estimated by the ^{13}C NMR spectra of copolymer, and assignment of each resonances and estimation of norbornene contents were according to the previous reports.[15,16]

Molecular weight and molecular weight distribution for polyethylenes and poly(ethylene-*co*-NBE)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from $<10^2$ to $< 2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Ethylene Polymerization, Ethylene/Norbornene (NBE) Copolymerization (MAO Cocatalyst). The typical reaction procedure for ethylene/norbornene copolymerization (Table 3, run 25) is as follows. Toluene (29.0 mL), *d*-MAO solid (145 mg, 2.5 mmol), and norbornene (15 mmol, 1412 mg) were added into the autoclave (100 mL scale, stainless steel) under stirring in the box. The reaction apparatus was then filled with ethylene at room temperature. A toluene solution, 1.0 mL containing **1** (1.0 μmol), was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 7 atm (ethylene pressure total 8 atm). The mixture was magnetically stirred for 10 min, the ethylene remaining was purged after reaction, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with EtOH, and was then dried in vacuo for several hours. The ethylene polymerization was carried out in the same procedure in absence of norbornene.

Ethylene Polymerization, Ethylene/Norbornene (NBE) Copolymerization (Et_2AlCl Cocatalyst). The typical reaction procedure for ethylene/norbornene copolymerization (Table 4, run 43) is as follows. Toluene (29.0 mL), Et_2AlCl solution (1.0 mol/L solution in *n*-hexane, 250 μmol), and norbornene (15 mmol, 1412 mg) were added into the autoclave (100 mL scale, stainless steel) under stirring in the box. The reaction apparatus was then filled with ethylene at 0 °C. A toluene solution (1.0 mL) containing **1** (0.05 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 7 atm (ethylene pressure total 8 atm). The reaction was terminated and the polymer was collected as the same procedure as described above for the copolymerization in the presence of MAO.

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Supporting Information Available: Figures showing additional ^{13}C NMR spectra for poly(ethylene-*co*-norbornene)s and poly(ethylene-*co*-1-hexene) prepared by **1**−cocatalyst systems and a ^{13}C NMR spectrum for the resultant polymer in an attempted ethylene/cyclopentene copolymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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